

Title: IMPROVED APPARATUS FOR DEHYDROGENATION OF ETHYLBENZENE TO
STYRENE

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1 BACKGROUND OF THE INVENTION

2 This invention relates to the field of styrene manufacture and more particularly discloses
3 apparatus including reactor vessels for the dehydrogenation of ethylbenzene into styrene
4 monomer.

5 It is well known in the art of styrene manufacture to react ethylbenzene over a
6 dehydrogenation catalyst such as iron oxide under elevated temperatures in the range of around
7 1000°F and at a pressure of about 10 to 20 PSIA in order to strip hydrogen from the ethyl radical
8 on the benzene ring to form the styrene molecule. This is normally done in a styrene radial
9 reactor which also is commonly termed an EB dehydro reactor. The dehydro reactors generally
10 are elongated cylindrical vertical structures of a very large size ranging in diameter from about
11 five to thirty feet or more and in length from about ten to one hundred feet or more. The normal
12 construction for such a reactor allows for input of the ethylbenzene gas at an inlet located in the
13 bottom center of the vertical reactor, whereupon the gas is flowed up through an annular area,
14 passing radially outward through a porous catalyst bed of iron oxide or other suitable dehydro
15 catalyst, and then passing upward through an outer annular area to exit at the top of the reactor
16 shell. Since the flow of ethylbenzene across the catalyst bed is in a radial direction, these reactors
17 are sometimes identified as "radial" reactors.

18 Normally a radial reactor would be sized such that the annular flow area inside the
19 catalyst bed would have some relative proportional value with respect to the cross-sectional flow

1 area of the inlet pipe delivering ethylbenzene to the reactor. Preferably the annular flow area
2 inside the catalyst bed would be larger than the cross-sectional flow area of the flow inlet pipe.
3 Because of the extended vertical length of such reactors, normally the inlet pipe to the bottom of
4 the reactor must come in at a relatively sharp ninety-degree radius and the resulting effect is a
5 side-to-side maldistribution of flow across the reactor vessel. Ideally, the inlet pipe to the reactor
6 would be a straight vertical pipe for a considerable distance prior to entering the reactor, but due
7 to physical configurations, this is not possible because of the extended vertical height of the
8 reactor.

9 Also, due to the nature of flow across the extended vertical length of the reactors,
10 switching from longitudinal or axial flow into radial or transverse flow and then back into
11 longitudinal flow, flow velocities across the catalyst bed from top to bottom vary widely in
12 conventional reactor vessels, thus resulting in degraded catalyst life in those areas of the reactor
13 with the greatest flow velocities. It has been found by experimentation and flow velocity
14 measurements that the highest feed velocity across the catalyst beds in a radial reactor generally
15 occurs near the top of the reactor, and the lowest velocity across the catalyst bed occurs near the
16 bottom of the reactor near the inlet pipe. This increased velocity at the top of the catalyst bed and
17 reduced velocity at the bottom of the catalyst bed results in a greatly shortened life of the catalyst
18 near the top of the reactor and forces a shutdown of the reactor for catalyst regeneration much
19 sooner than normally desirable.

20 Accordingly, it is desirable to improve the flow in the reactor both in the axial and
21 vertical directions. U.S. Patent No. 5,358,698 to Butler et al. issued on October 25, 1994 and is
22 assigned to Fina Technology, Inc. This '698 patent discloses a method for improving the flow in
23 a dehydrogenation reactor by using a displacement cylinder. The disclosure of this patent is

1 hereby incorporated by reference in its entirety. While improvement in fluid flow is achieved by
2 the method taught in the '698 patent, further improvements were needed in order to improve the
3 efficiency of the catalyst.

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5 **SUMMARY OF THE INVENTION**

6 The present invention discloses a dehydrogenation reactor vessel apparatus that
7 comprises a displacement cylinder and utilizes specific baffling on the exterior of such
8 displacement cylinder to reduce the vertical flow differences across the reactor height. The
9 baffles are attached to the displacement cylinder without having to disassemble the reactor. The
10 baffles are attached to the exterior of the displacement cylinder at specific locations to reduce the
11 flow rate in the higher flow rate regions of the reactor. In one embodiment, at least two baffles
12 are added to the top half of the reactor to allow more uniform fluid flow through the reactor.

13 In accordance with one embodiment of the present invention, an existing ethylbenzene
14 dehydrogenation reactor is retrofitted to improve fluid flow and extend catalyst life. Retrofitting
15 the reactor starts with analysis of existing reactor condition and catalyst loading. The fluid flow
16 through the reactor is simulated. Once simulated conditions reflect actual operations, fluid flow
17 improvements are simulated. The improvements comprise adding baffles to the displacement
18 column at locations exhibiting higher fluid flow velocities. The location, size and number of
19 baffles are determined by simulation to provide as uniform a fluid flow as possible. After
20 simulation, the actual baffles are added to the outside of the displacement column without
21 disassembly of the reactor. The baffles are preferably added to the top half of the reactor and do
22 not extend more than half the distance from the displacement reactor to the inner wall of the
23 catalyst bed. The process results in optimization of pressure drop while minimizing the same.

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2 BRIEF DESCRIPTION OF THE DRAWINGS

3 **Figure 1** illustrates a cross sectional schematic diagram of the reactor vessel and baffles
4 location in accordance with one embodiment of the present invention.

5 **Figure 2** shows the normalization of fluid flow in one reactor modified in accordance
6 with the present invention.

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8 DETAILED DESCRIPTION

9 As has been the trend in the industry, larger reactors for the manufacture of styrene are
10 utilized in order to reduce operating costs. While the present invention is described relative to an
11 ethylbenzene dehydrogenation reactor to form styrene, the invention is applicable to improving
12 the operations of large reactors with fixed catalyst beds.

13 **FIG. 1** is a schematic cross sectional side view of an EB dehydro reactor vessel 10
14 having an elongated outer cylindrical shell 11 enclosing an inner cylindrical displacement
15 member 12 located concentrically inside cylindrical vessel 11. Vessel 11 and displacement
16 member 12 are generally right circular cylinders, meaning that a cross sectional view taken
17 perpendicular to the longitudinal center lines of these two vessels would be circular in shape.
18 Preferably, displacement cylinder 12 is located co-axially within vessel 11, meaning that the
19 central longitudinal axis of the two cylindrical structures coincide. An inlet pipe 13 having a
20 large cross sectional area is connected to a central inlet opening 14 formed in the bottom of shell
21 11. Preferably inlet pipe 13 is also cylindrical in cross sectional area.

22 The placement of cylinder 12 within vessel 10 in a coaxial alignment serves to form an
23 annular catalyst area 18 around the displacement cylinder. A series of optional radially

1 outwardly extending flow baffles may be formed on the outer wall of catalyst bed, extending
2 radially outward therefrom to further direct flow of gases flowing through the catalyst bed and
3 directing them into a radial flow direction, thereby preventing longitudinal flow and further
4 smoothing out flow across the catalyst bed. Once these catalyst bed baffles are installed, the
5 locations cannot be changed without long downtime and disassembly of the reactor.

6 The catalyst bed 18 comprises a concentric cylindrical catalyst shell made of a perforated
7 or porous inner wall and a similar porous or perforated outer wall. Preferably, the catalyst shell is
8 sufficient to maximize flow and still retain the dehydro catalyst between the inner and outer
9 walls. Some typical catalysts utilized in the dehydrogenation process are those sold by United
10 Catalyst (Styromax series) and by Criterion (such as Versicat series). These may be of the iron
11 oxide type or other dehydrogenation types of catalysts. The shape and size of the catalyst
12 particles varies and may have an effect on the fluid flow in the reactor.

13 The sizing of the flow areas of the inlet pipe 13 and the annular area 21 (inner annulus)
14 between the displacement cylinder 12 and the catalyst bed 18 is preferably in the range of about
15 2 to 1 with annular area 21 being approximately twice the value of the cross sectional area of
16 pipe 13. Furthermore, the annular area 22 (outer annulus) between catalyst bed 18 and vessel 11
17 is relatively narrow and would not allow sufficient space for later modifications or work in the
18 area. To perform any work on the interior of the vessel wall 11, the catalyst bed 18 must be
19 removed. This represents significant cost and long downtime. Outlet pipe 5 and opening 6
20 provide the means for removal of product from the reactor. Baffles 30, 31, and 32 are shown in
21 accordance with one embodiment of the present invention. These baffles affect the flow through
22 the reactor and do not operate to achieve the same function of any baffles that may be present in
23 the inlet pipe 13 or baffles on catalyst trays.

1 The present invention is particularly suitable for the modification of existing reactors as
2 can be seen from the following discussion. For an existing reactor, a steady state flow simulation
3 is conducted in accordance with well known methods. In one embodiment, a cold flow is
4 conducted using a two-dimensional axis-symmetric reactor model. The geometry is divided into
5 about 14,000 hexahedral cells. Average values for temperature, molecular weight and specific
6 heats were utilized from actual historical data at the affected plant. Table 1 below shows typical
7 operating conditions.

Table 1

Flow, lb./h	500,000
Exit pressure, psia	8-14
Average temperature, °F	> 1000
Average molecular weight	25.9 – 26.2
Average viscosity, cp	0.003
Average specific heat, J/Kg.°C	2400-2500

Catalyst bed porosity was also considered. This took into account the shape and particle size of the catalyst. Various catalysts were considered, including smooth, shaped and ribbed versions. Catalyst pellet diameter ranged from 3-3.5 millimeters (mm) with pellet length from 4-9 mm. The catalyst bed densities varied from 70 to 95 pounds per cubic foot. The catalyst bed porosity changes during reactor operations, achieving its lowest value at end-of-run operation.

15 The velocity profile and pressure was calculated for each cell within the reactor
16 geometry. Calculations for fluid flow simulations are well known in the art and the methods to
17 achieve such are not subject of this invention.

Flow distribution for a reactor similar to that shown in Figure 1, but without baffles 30,
31 and 32, showed that the top 20% and the bottom 20% of the reactor bed operated at higher
than normal LHSV. On the other hand, the middle 60% operated at lower than normal LHSV.

1 Thus, flow as a function of distance decreased in the bottom half of the reactor and increased in
2 the top half of the reactor. The increase in the flow in the top half is attributed to the higher
3 pressure drop in the outer annulus as compared to that in the inner annulus. At the bottom half,
4 the increased flow was attributed to excessive inner annulus pressure drop as compared to the
5 outer annulus.

6 It was determined that for a retrofitting of an existing reactor, the best approach to correct
7 the fluid flow was to place baffles of specified size at specific heights on the displacement
8 cylinder to provide as close to uniform flow through the reactor. Adding rings or baffles in the
9 top section of the inner annulus increased the inner annulus pressure drop to match the pressure
10 drop in the outer annulus. Catalyst bed fluidization was taken into account in the placement and
11 number of baffles or rings. Some of the requirements of the present invention include the
12 optimization of pressure drop in addition to minimization of pressure drop. In other words, the
13 addition of baffles increases the pressure drop in the reactor. The addition of the baffles should
14 be done with minimal increase in pressure drop and maximum effect on fluid flow
15 normalization. Additionally, it is preferred that the baffles extension into the reactor is limited to
16 not exceed half the distance from the outer wall on the displacement cylinder to the inner wall of
17 the catalyst bed, i.e., half the width of the inner annulus. This combination of factors is included
18 in the simulation solution for fluid flow normalization.

19 The addition of baffles or rings on the outer surface of the displacement cylinder
20 (cylinder 12) allows the modification of the reactor fluid flow without having to take out the
21 displacement cylinder or the catalyst trays or structure. The displacement cylinder is of
22 sufficient width that a man way is cut into the top and work is performed from the inside of the
23 displacement cylinder. The cylinder wall is cut at the required location and the baffles are added

1 and welded from the inside. This does not require any dismantling of the reactor and the changes
2 can be made with minimum down time.

3 In accordance with one embodiment of the present invention, an existing ethylbenzene
4 dehydrogenation reactor was analyzed and modified. The reactor space was 62 feet in height
5 with a 60 inch diameter inlet and an 88 inch diameter outlet. The reactor had an inside diameter
6 of 13.5 feet. The outside diameter of the displacement cylinder was 5.75 feet. The catalyst bed
7 had an inner diameter of 7 feet and 5.25 inches and an outer diameter of 12.5 feet. The reactor
8 had an outer annulus of 6 inches depth. In operation, this reactor had a flow rate of over 500,000
9 pounds per hour. As can be seen from the dimensions, the available space inside the reactor does
10 not allow room for individuals to work in the available space. Any modification to the system
11 would require dismantling of the reactor. This has been the case until the present invention. To
12 improve the fluid flow of this reactor according to its operating parameters, three baffles or rings
13 were installed on the outer surface (reaction side) of the displacement reactor. The baffles are
14 shown as items 30, 31 and 32 in figure 1. The top ring 30 was installed at a height of 49 feet and
15 extended 7.5 inches into the reactor. The middle ring or baffle 31 was installed at a height of
16 46.75 feet and extended 6.25 inches into the reactor. The bottom ring 32 was installed at a
17 height of 40 feet and extended 5.0 inches into the reactor. These baffles resulted in a more
18 uniform flow of fluid through the reactor. As can be seen, the baffles were added to the top half
19 of this reactor with increasing extension to the reactor as height in the reactor is increased. The
20 improvement in the fluid flow uniformity resulted in increased catalyst life and efficiency.

21 **Figure 2** shows the effect of adding the baffles in the above example. The solid line
22 shows the fluid flow in the vertical direction through the reactor prior to the addition of the
23 baffles. The graph shows the above normal fluid flow at the lower part of the reactor and the top

1 part. The addition of the baffles resulted in normalizing the flow at the top (location of the
2 baffles) and improving fluid flow through the middle.

3 Thus, the present invention, as disclosed in the aforementioned drawings and descriptions
4 corresponding thereto, provides means and apparatus for the dehydrogenation of ethylbenzene to
5 styrene, which process and apparatus enjoys the advantages of extended catalyst life and closer
6 control of flow velocities at various points up-and-down the reactor cross-sectional
7 configuration. Conventional reactors suffer from short catalyst life due to non-consistent flow
8 velocities across varying sections of the catalyst beds.

9 It was also discovered that flow velocities through the top of the catalyst bed were in the
10 range of one and one-half to two and one-half times higher than those across the middle of the
11 bed. Thus, it was realized that utilization of the catalyst in the reactor was far from uniform,
12 which in turn contributed directly to much shorter than expected catalyst life.

13 As a result, the present invention discloses reactor configurations that significantly reduce
14 the vertical flow velocity variations. This is achieved by the use of baffles along the exterior wall
15 of the displacement reactor. Flow simulations are utilized to determine the number, location and
16 size of the baffles.

17 In typical operation, ethylbenzene feedstock is supplied to the reactor vessels via feed
18 supply line 13 through inlet area 14. From there the feed material flows into the reactor around
19 the catalyst beds 18. Operating conditions in the reactor are preferably in the range of about
20 900° to 1225° F temperature, and about 8-22 PSIA pressure. Flow velocities in the reactor range
21 from about 100 to 400 fps, with a preferred overall flow velocity through the reactor of around
22 200 to 300 fps.

1 Although certain preferred embodiments of the present invention have been herein
2 described in order to provide an understanding of the general principles of the invention, it will
3 be appreciated that various changes and innovations can be effected in the described
4 dehydrogenation reactor assembly without departing from these principles. For example,
5 whereas the preferred embodiment is described as adding three baffles at the top half of the
6 reactor, the number and location of the baffles may vary depending on the particular reactor.
7 Also, it is apparent that different baffling shapes could be utilized to achieve flow normalization.
8 Other changes would be apparent to one skilled in the art and therefore the invention is declared
9 to cover all changes and modifications of the specific examples of the invention, herein disclosed
10 for purposes of illustration, which do not constitute departures from the spirit and scope of the
11 invention.

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